FILTERING UNSATURATED HYDROCARBONS USING INTERMETALLIC NANO-CLUSTERS

Ins. A'

FIELD OF THE INVENTION

The invention relates to filtering of unsaturated hydrocarbons from mainstream cigarette smoke using intermetallic nano-clusters. The nano-clusters can

5   be incorporated in cigarette filter elements in a manner which selectively removes gaseous components such as 1,3-butadiene, isoprene, toluene and the like from mainstream smoke.

BACKGROUND OF THE INVENTION

Fresh activated carbon can be used to reduce the level of 1,3-butadiene in mainstream cigarette smoke. However, because activated carbon is a broad base

10   physical adsorbent of gaseous compounds and removes a large number of volatile and gas-phase compounds from cigarette smoke, the result can produce undesired effects on the flavor of the tobacco smoke. Selective filtration, on the other hand, has the advantage of removing targeted gaseous compounds while minimizing the effect on flavor of the tobacco smoke.

Ins B' SUMMARY OF THE INVENTION

15   According to the invention, small (nanometer or micrometer size) metal or metal alloy clusters can be incorporated in or on a support media (e.g., silica gel, porous carbon, zeolites, etc.) and the resulting filter material can be used to selectively bind to unsaturated hydrocarbons present in cigarette smoke. In a preferred embodiment, transition metals and metal alloys incorporated into the

20   clusters can be used to remove gaseous components such as 1,3-butadiene from mainstream cigarette smoke as it passes through a filter containing the supported reactive metal clusters. The transition metals can include iron and titanium and alloys containing such elements such as iron alloys, titanium alloys, intermetallic compounds such as iron aluminide or titanium aluminide or transition metal salts

(e.g., Cu, Fe, Zn, Al, Ce, V sulfates and/or phosphates) on high surface area support materials.

Using state-of-the-art theoretical techniques based on density functional theory and generalized gradient approximation for exchange and correlation potential, calculations of the binding energies of trans- and cis-form of butadiene to transition metal atom (Fe) as well as dimers (Fe_2, FeAl, and Al_2) were carried out. The objective of the study was to understand if (1) butadiene binds to these species and, if so, how the binding varies from one atom to another, (2) if one form of butadiene binds more strongly than the other, (3) where do the metal atoms insert and (4) if the structure of butadiene undergoes geometrical transformation as it binds to metal atoms. The study was carried out to see if suitable traps can be found for this organic molecule and to suggest experiments to prove the theoretical predictions.

(1) Geometry of cis- and trans-butadiene as they interact with metal atoms and dimers

In FIG. 1(a) the trans form of butadiene is given. It is a planar molecule. An Fe atom inserts into the C-H bond and gains an energy of 0.37 eV (see Table 1) over an isolated trans-butadiene and Fe atom. While interacting with the cis-form (FIG. 2), the Fe atom, on the other hand, attaches to the C-C double bond and the structure becomes three-dimensional. Energetically, the Fe-butadiene complex in the cis-form is more stable than the trans-form by 0.78 eV. This is particularly interesting as the trans- and cis-forms of butadiene are energetically nearly degenerate. Addition of Fe does seem to break this degeneracy.

Fe_2 does not bind to the trans- or cis-form of butadiene (FIG. 1(c)) as energetically this is higher than dissociated Fe_2 and butadiene. FeAl and Al_2 dimers, on the other hand, bind strongly to both the trans- and cis-forms of butadiene. While the bond between Fe and Al remains intact (see FIG. 1(d) and 2(c)), that between Al and Al breaks (see FIG. 1(e) and 2(d)). This is because the Fe-Al bond is stronger than the Al-Al bond. Nevertheless, a binding energy in excess of 1eV between a

metal dimer and butadiene is sufficient. The C-C and C-H bonds in butadiene do not change appreciably as metal atoms are bound to the molecule.

(2) <u>Binding of metal atoms to C_2 and C-H dimers</u>

From the above discussion it is apparent that a metal atom either inserts into the C-H bond or attaches to a C-C bond in butadiene. As calculations presented in FIG. 1 and FIG. 2 and Table 1 are very complex and costly, the systematics of transition metal binding to CH and C_2 molecules was studied to see which atoms can possibly bond more strongly to butadiene than Fe. The corresponding energies are given in Table 2. The data indicates that Sc, Ti, V, Co, and Ni are better candidates than Fe whether they prefer to insert into the CH bond or attach to C-C bond. Calculations of Sc, Ti, V, Co, and Ni interacting with the complete butadiene molecule can be carried out to prove this hypothesis. Experimental studies of transition metal atoms and Al reacting with butadiene in the gas phase can also be carried out.

Table 1		
Binding Energy (eV)		
System	Trans (FIG. 1)	Cis (FIG. 2)
C_4H_6	43.98	43.82
C_4H_6Fe	0.37	1.15
$C_4H_6Fe_2$	-	-
C_4H_6FeAl	1.35	1.76
$C_4H_6Al_2$	2.22	2.03

$E_b(C_4H_6) = E(C_4H_6) - 4E(C) - 6E(H)$
$E_b(C_4H_6Fe) = E(C_4H_6Fe) - E(C_4H_6) - E(Fe)$

$E_b(C_4H_6FeAl) = E(C_4H_6FeAl) - E(C_4H_6) - E(FeAl)$
$E_b(C_4H_6Al_2) = E(C_4H_6Al_2) - E(C_4H_6) - E(Al_2)$

$E_b(Al_2) = E(Al_2) - 2E(Al) = 1.76eV$
$E_b(FeAl) = E(FeAl) - E(Fe) - E(Al) = 2.53eV$

E = total energy, kE_b = binding energy

Table 2		
Energetics of M-C_2 and M-CH (M = Sc...Ni) in eV		
M	$E_b(MC_2)$	$E_b(MCH)$
Sc	6.76	9.02
Ti	6.95	6.21
V	7.28	4.95
Cr	4.37	4.08
Mn	5.03	3.61
Fe	4.86	4.68
Co	6.16	5.45
Ni	6.74	5.79

$E_b(MC_2) = E(MC_2) - E(M) - E(C_2)$
$E_b(MCH) = E(MCH) - E(M) - E(CH)$

Clusters of nanosize intermetallic powders such as Fe_3Al, FeAl, TiAl, NiAl and Ni_3Al can be obtained by melting and atomization techniques. They can be processed by laser evaporation, and or chemical decomposition techniques. The powders can be produced in inert atmospheres such as argon or helium, or by bleeding a certain amount of oxygen, nitrogen, or ammonia to alter the surface property of the powders. The sizes of the particles may be altered by the residence time of the laser pulse, cooling time, temperature, etc. For instance, it is possible to synthesize nanoparticles of controlled size and composition using pulsed laser vaporization with controlled condensation (LVCC) in a diffusion cloud chamber under well-defined conditions of temperature and pressure.

While the invention has been described in detail with reference to specific embodiments thereof, it will be apparent to those skilled in the art that various changes and modifications can be made, and equivalents employed, without departing from the scope of the appended claims.